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PHOTOCHEMICAL STUDIES
OF
SECONDARY NITRAMINES I. ABSORPTION
SPETRA OF NITRAMINES AND PHOTOLYSIS
OF
DIMETHYLNITRAMINE IN SOLUTION

K. SURYANARAYANAN
SURYANARAYANA BULUSU

SEPTEMBER 1970

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PHOTOCHEMICAL STUDIES OF SECONDARY NITRAMINES 1. ABSORPTION
SPECTRA OF NITRAMINES AND PHOTOLYSIS OF DIMETHYLNITRAMINE
IN SOLUTION

by

K. Suryanarayanan
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Explosives Laboratory
Feltman Research Laboratories
Picatinny Arsenal
Dover, New Jersey 07801

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ABSTRACT

This report reviews the absorption spectra of several nitramines and gives new spectra for dimethylnitramine, RDX, and HMX. It also deals with the photolysis of dimethylnitramine in alcohol solution.

Solvent shifts in the absorption spectra support the conclusion that dimethylnitramine undergoes a $\pi-\pi^*$ electronic transition caused by intense absorption in the near UV (240 nm) and exhibits weak absorption in n-hexane up to 318 nm, probably due to excitation of nonbonding electrons in the nitramino group. Although the solvent chosen for this study was ethyl alcohol, some data are presented from photolysis in acetonitrile and n-hexane, as well as from irradiation in the solid form. G.C., NMR, IR, and UV techniques were used for product analysis. The major photolysis product of dimethylnitramine under the experimental conditions used appears to be N-nitrosodimethylamine, as in gas-phase thermal decomposition. In alcohol solution, its rate of formation increases considerably and later levels off with increasing initial concentration of dimethylnitramine. The overall photodecomposition is compared with previous thermal decomposition and electron-impact fragmentation data in terms of bond-breaking steps. Quantum yields for disappearance of dimethylnitramine and formation of nitrosamine are 0.3 and 0.1, respectively.

INTRODUCTION

The photochemistry of nitramines seems to have received little attention in the past although a survey of literature revealed photolytic studies of numerous nitro-substituted compounds. As a part of a wider study of the decomposition chemistry, investigations of photolysis and radiolysis of the secondary nitramines, HMX and RDX, have been begun in the Explosives Laboratory at Picatinny. These compounds are being given primary emphasis in the current program because of their obvious importance¹ to the explosives field (Ref 1). In particular, the effects of irradiation on impact sensitivity are of considerable importance (Ref 2). In addition to HMX^a and RDX^a, the structurally simpler dimethylnitramine has also been chosen for

^a In the explosive field, 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane and 1,3,5-trinitro-1,3,5-triazacyclohexane are known, respectively, as HMX and RDX.

the initial studies. In this report the ultraviolet spectra of nitramines in general, and the preliminary results of dimethylnitramine photolysis, both in solution, will be described. The photodecomposition will be compared with the earlier investigation of thermal decomposition (Refs 3-5) and electron-impact fragmentation (Ref 6) of this compound. Photolysis of HMX-polymorphs and RDX in the polycrystalline form will be discussed in a later report which will follow shortly.

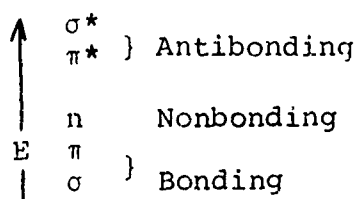
Photochemical reactions mostly require absorption of ultraviolet or visible light in the 200-800 nm wavelength range. This corresponds to an energy absorption of 1.7 to 6.5 eV (40-150 Kcal/mole) by each molecule giving rise to electronic excitation. Energetically, this is well above the range of thermally induced reactions. It is useful, therefore, to understand the general properties of the electronically excited states of the material under study. These states which have an altered distribution of valence electrons often give rise to chemical reactions different from the ground state. The molecular electronic transitions and their chemical consequences can be better characterized by a study of photolysis in solution. The reacting molecule in solution is free from the geometric effects of the lattice in the solid state. When it is part of an ordered crystal lattice, the latter introduces topochemical effects such as anisotropy of light absorption and polymorphic differences in neighboring group interactions. In addition, lattice imperfections of all types create local perturbations that determine the fate of the excited molecule. The geometry of the crystal lattice may effect the chemical end-product. A study of the solution chemistry was therefore considered useful for comparison.

ULTRAVIOLET SPECTRA OF NITRAMINES AND RELATED COMPOUNDS IN SOLUTION

The absorption spectra of a variety of nitramines, some of which contain additional functional groups, had been reported by several authors (Ref 7-9). The λ_{max} and ϵ_{max} values for some of these spectra are collected together in Table I for convenience in discussion. In particular, the spectra of HMX, RDX, and some primary nitramines and nitrosamines are included. The discussion will be confined essentially to absorption bands appearing above 220 nm wavelength, which was the region of interest in the photolysis studies to be described here.

Characterization of Electronic Transitions

Since the different electronic distributions of the ground and the excited states (Ref 11) lead to different reactivities, it is useful to first identify the electronic transition responsible for a given photochemical process. The electronic states of organic molecules can be conveniently considered in terms of one-electron transitions within the five common molecular orbitals. These orbitals formed by the combination of atomic s, p, or mixed (hybrid)s-p orbitals are shown below:



The nonbonding electrons, such as the lone pairs attached to N and O atoms, occupy p-orbitals and may sometimes take part in bond formation to a degree dependent on the orbital symmetry.

The above picture of the orbital levels is helpful in relating the absorption bands in the spectra to the transition energies. Since σ , π , and n represent the order of filling the ground state levels, 'n' is farthest from the nucleus and easiest to perturb. Transitions from the σ -level ($\sigma \rightarrow \sigma^*$) require high energy and occur only in the vacuum UV region, which is not relevant to the present studies. The interaction between σ and π levels is usually negligible. The $n \rightarrow \sigma^*$ transitions also occur generally below 200 nm except in halogenated compounds where they shift to a somewhat higher wavelength (250 nm). The $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are the most common in organic chromophores containing both nonbonding and π electrons such as the NO_2 group. These two (and the $n \rightarrow \sigma^*$ transition where possible) cause most of the observed photochemical effects in the near-UV and visible regions. The $\pi \rightarrow \pi^*$ transition which requires relatively more energy than the $n \rightarrow \pi^*$, occurs near 200 nm but moves to longer wavelengths if the molecule has conjugation or groups with strong inductive effect and, generally, is an allowed and intense absorption. The $n \rightarrow \pi^*$ transition is forbidden and is usually weak but because of its low energy requirement occurs readily in molecules containing hetero atoms causing many

of the photochemical reactions.

The usually nonoverlapping nature of the n and π orbitals makes for very effective unpairing of the nonbonding electrons, radical-like reactivity of the species, and small singlet-triplet splitting. Even though the nodal plane is perpendicular to the bond axis, the π^* orbital, overlaps the π orbital sufficiently that the upper state behaves very much less like a species containing an unpaired electron. In some molecules where such overlap is minimal, a diradical nature is manifested also.

Effects of Solvents on Energy of Transition

The higher electronic states are more readily polarizable than ground state; therefore, they are subject to greater interaction with the solvent. This difference in solute-solvent interaction affects the wavelength of absorption as well as the structure of the bands, and serves as a way of characterizing the transition.

Nonpolar solvents merely lower the transition energy of the molecule in solution slightly relative to the gas phase. Polar solvents show a stronger effect attributed to the dipole polarization and hydrogen-bonding effects. The nature and magnitude of the effect depend on the particular transition as well as the polar nature of the solute molecule. In the case of an $n \rightarrow \pi^*$ transition, solvent hydrogen-bonding is stronger in the ground state than in the excited state and, therefore, more energy is required. Thus the absorption band undergoes a blue shift with increasing solvent polarity. Hydrogen bonding has the opposite effect on a $\pi \rightarrow \pi^*$ transition in that it stabilizes the excited state much more than the ground state. The result is a red shift of the absorption band in more polar solvents. In general, greater interaction of the excited state with polar solvents also causes a loss of vibrational structure.

Discussion of the Absorption Spectra

The absorption spectra of the compounds shown in Table 1 will now be discussed in terms of the solvent shifts which have not already been considered in earlier reports. This will, hopefully, provide a basis for a first-order comparison of nitramines and other nitro compounds in terms of their photochemical reactions. Figures 1 to 4 show the spectra obtained in this work for RDX, HMX, and dimethyl-

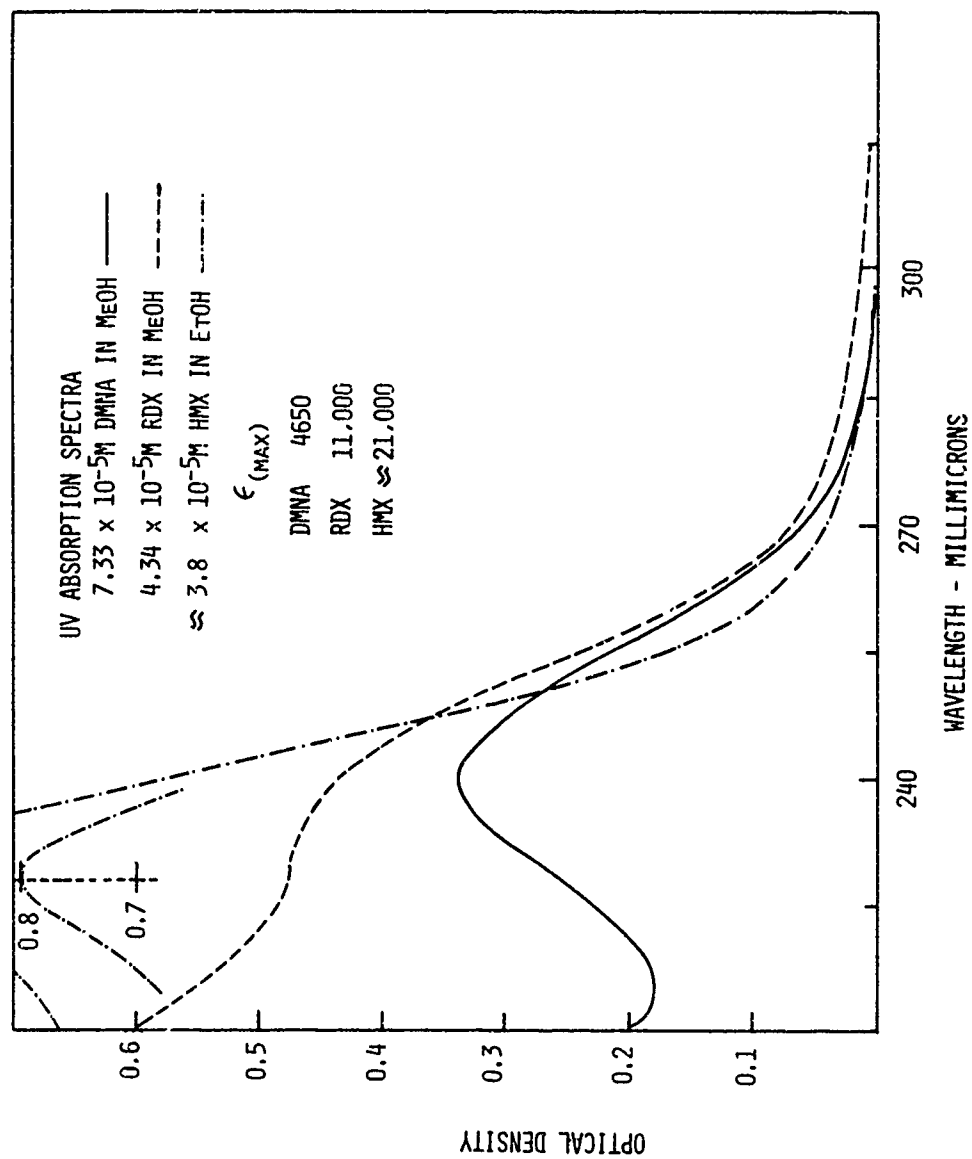


Fig 1 Ultraviolet absorption spectra of DMNA and RDX in MeOH, and of HMX in EtOH

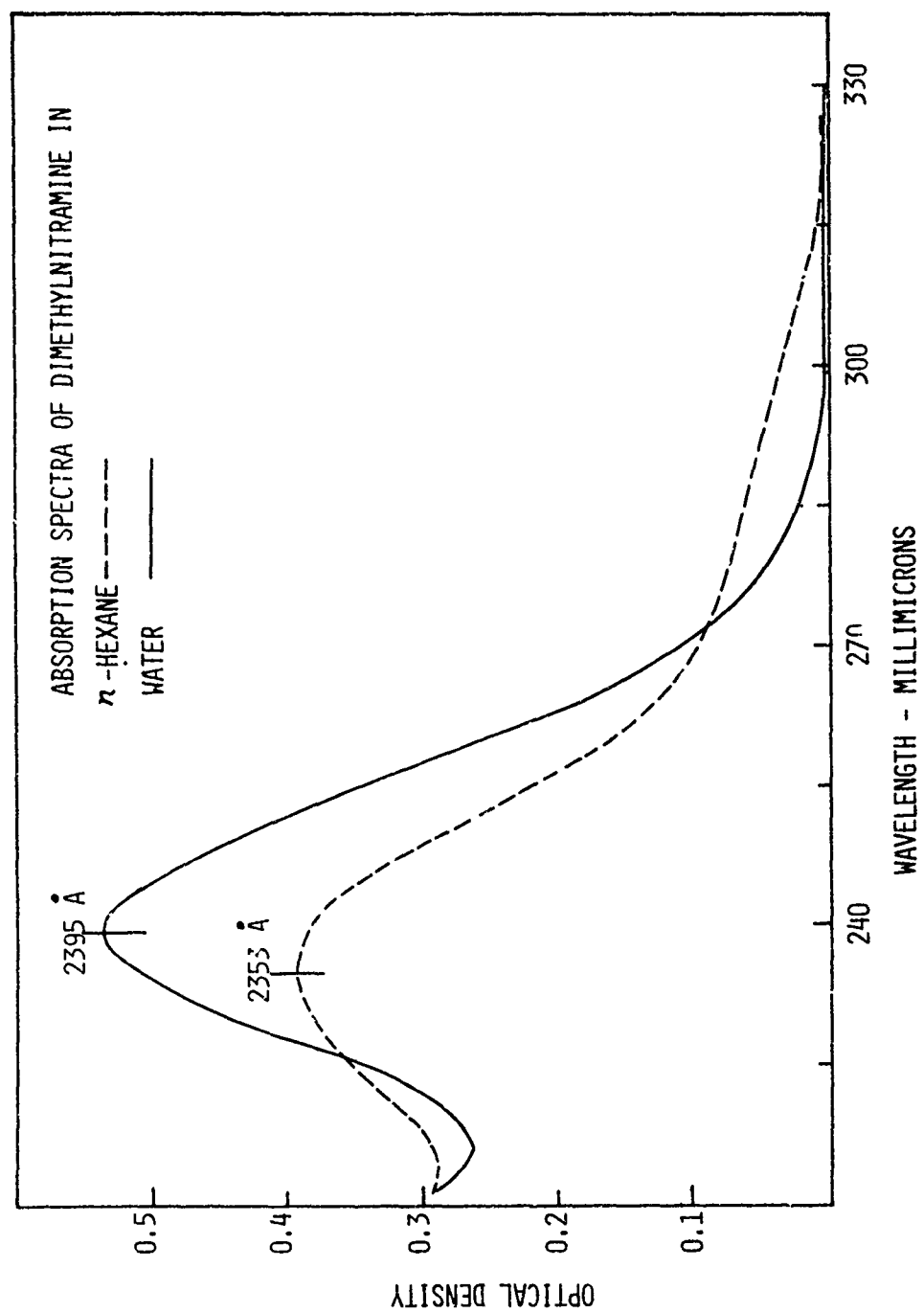


Fig 2 Absorption spectra of DMNA in n-hexane and water

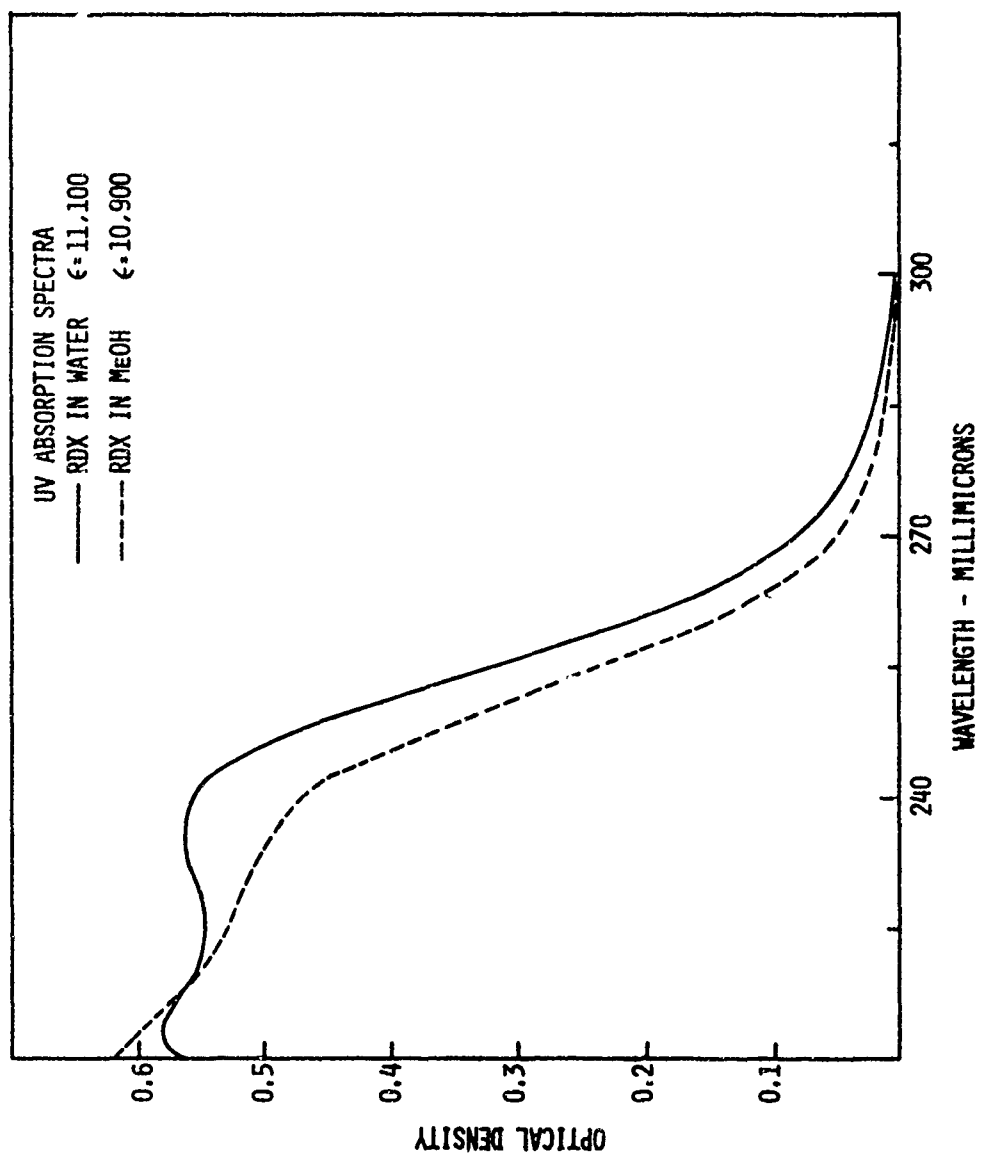


Fig 3 Absorption spectra of RDX in MeOH and water

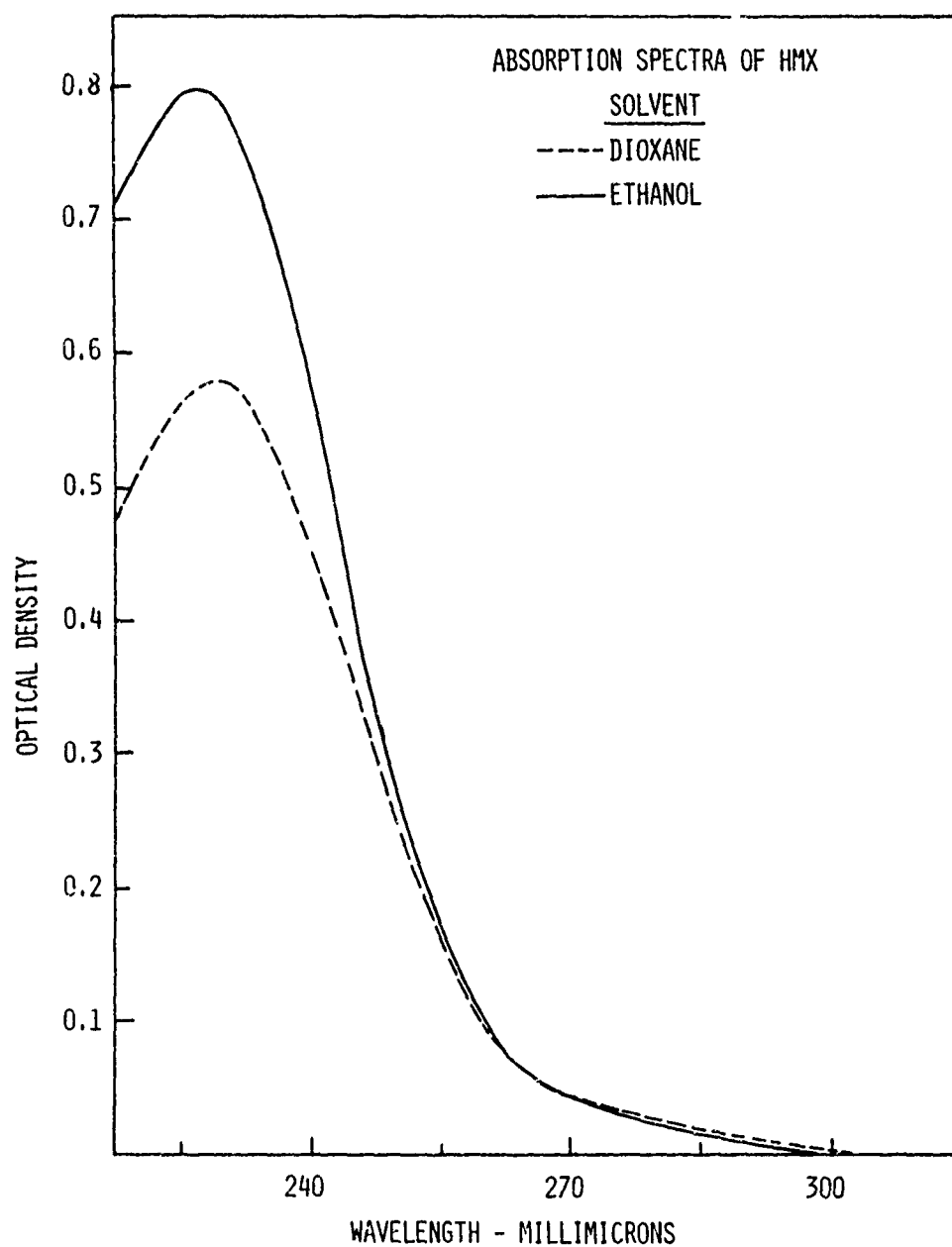


Fig 4 Absorption spectra of HMX in dioxane and ethanol

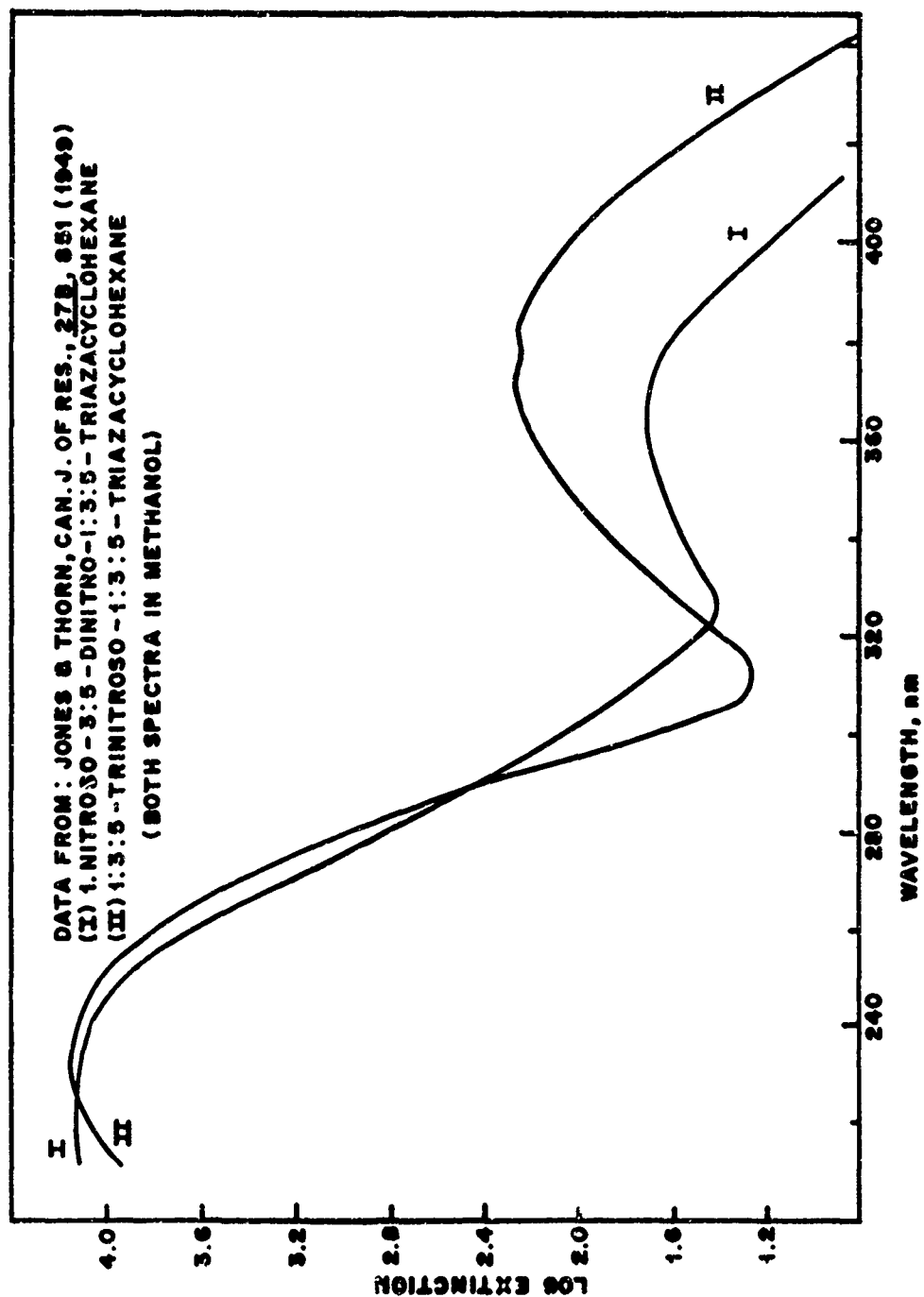
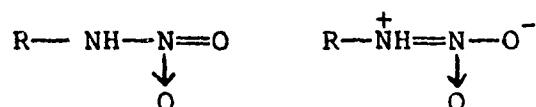


Fig 5 Spectra of (I) 1-nitroso - 3:5-dinitro-1:3:5-triazacyclohexane and of (II) 1:3:5-trinitroso-1:3:5-triazacyclohexane, both in methanol

nitramine in various solvents.

The primary nitramines illustrated in Table 1 do not show a low-energy transition seen in the nitrosamines. This transition occurs in nitrosamines at about 345 nm and has been attributed to the symmetry forbidden $n \rightarrow \pi^*$ excitation. The nitramines exhibit strong absorption near 225 - 230 nm. In two examples, alkali shifted this band towards red by 60 to 70 angstroms but methylnitramine showed only a slight red shift. The effect of alkali must be due to ionization of the nitramine group. As a consequence of the enhanced resonance in the $\text{NH}-\text{NO}_2$ group, the energy



for the $\pi \rightarrow \pi^*$ transition will be lowered. The intensity of absorption is highly consistent with a $\pi \rightarrow \pi^*$ transition. Generally, polar solvents have either little effect or a lowering effect on the wavelength and this is borne out by these spectra.

Dimethylnitramine

The red shift of 42 angstroms observed in changing the solvent from *n*-hexane to water (see Figure 2) was higher than that previously reported (Ref 9). However, the previous estimate of 20 angstroms (Table 1) was based on a spectrum in dioxane from Reference 7 and one in water from Reference 10. It is noteworthy that the absorption intensity falls considerably in going from water to *n*-hexane and methanol. The red-shift is consistent with the assignment (Ref 9) of this band chiefly to a $\pi \rightarrow \pi^*$ transition in the $\text{N}-\text{NO}_2$ chromophore. On the basis of molecular orbital calculations, Stals (Ref 9) suggested that four absorption bands at 292, 240, 238, and 193 nm contribute to the observed absorption envelop with a maximum at 240 nm in water. According to these calculations, the transition at 240 nm is a combination of $\pi \rightarrow \pi^*$ and $(\pi \sigma \rightarrow \sigma_{\text{CNC, NO}_2}^*)^a$. The calculated oscillator strength^b of the band at 292 nm was half that of the one at 240 nm. While the spectra in

^aThis is promotion of an SP^2 nonbonding electron to a σ^* -antibonding orbital.

^bOscillator strength is a measure of the integrated molar extinction coefficient of the absorption band and thus would be proportional to the area under the curve for a given band.

water and dioxane do not show this absorption, the n-hexane solution does show a substantial absorption tail ending at 218 nm. This band would be expected to shift to higher energy in polar solvents whether it is due to the $n \rightarrow \pi^*$ transition or to an $n \rightarrow \sigma^*$ excitation as assigned by Stals. By analogy with nitrosamines (Refs 7,8), it would be assigned to an $n \rightarrow \pi^*$ transition. Since the calculated oscillator strength of the band at 292 nm (4.25 ev) was nearly half that of the one at 240 nm, it may be consistent with an $n \rightarrow \pi^*$ transition. The observed much smaller extinction in the absorption edge of the spectrum appears more likely to be $n \rightarrow \pi^*$ excitation. It is not possible to distinguish between them easily except indirectly by photochemical experiments.

RDX and HMX

Because of the lack of a distinctive maximum (Fig 3), it is difficult to observe any solvent shift in RDX spectra. The new spectra of HMX shown in Figure 4, which were obtained in dioxane and ethanol solutions, indicate a small but clear red shift of 30 angstroms in the more polar solvent, ethanol. This confirms Stals' assignment of the band at 227 nm to a $\pi \rightarrow \pi^*$ electronic transition.

If one of the nitro groups in RDX is replaced by a nitroso group (see 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane in Table 1 and Fig 5) the $n \rightarrow \pi^*$ excitation band appears at 370 nm⁷. Polar solvents shift this to a shorter wavelength, as may be seen clearly in the table. Likewise, dimethyl nitrosamine exhibits a single band at 345 nm in alcohol (in addition to the one at 231 nm) which shifts to a longer wavelength in the less polar solvent, n-hexane (361 nm) and also shows considerable vibrational structure. (Refs 12,13); (see Table 1).

It is thus clear that the principal effect of absorption of 253.7 nm light by dimethylnitramine in ethyl alcohol is a $\pi \rightarrow \pi^*$ electronic transition. Irradiation in hydrocarbon solvents near 300 nm may result in a weak band due to an $n \rightarrow \pi^*$ excitation. The same applies to HMX and RDX also.

PHOTOLYSIS OF DIMETHYLNITRAMINE

A literature survey revealed no detailed studies of the photolysis of nitramines although considerable work

Table 1 Ultraviolet absorption bands of nitramines and nitrosamines in different solvents

Compound	Solvent*	λ_{\max} (nm)	ϵ_{\max}	Reference
<u>Primary Nitramines</u>				
CH ₃ NHNO ₂	C ₂ H ₅ OH	420 (325sh)		7
	H ₂ O	230	7,210	7
	HCl, 5x10 ³ N	232.5	7,200	7
	KOH, 0.25N	228	7,600	7
CH ₂ (NHNO ₂) ₂	C ₂ H ₅ OH	226	12,530	7
	NaOH, 0.2N	233	17,100	7
-(CH ₂ NHNO ₂) ₂	C ₂ H ₅ OH	232	12,000	8
		230	13,400	7
	NaOH, 0.2N	236	17,100	7
<u>Secondary Nitramines</u>				
(CH ₃) ₂ NNO ₂	Dioxane	240	6,300	7
	H ₂ O	238	8,000	10
	H ₂ O	239.5	7,400	This
	MeOH	240	4,620	Report
	n-Hexane	235.3	4,750	
RDX	C ₂ H ₅ OH	213	11,000	8
	CH ₃ OH	230 Broad	11,200	7
	H ₂ O			
	CH ₃ OH	204	13,100	9
		234sh		9
		237		9
	CH ₃ OH	225-230	11,000	This
	H ₂ O	237	11,100	Report
HMX		213	11,400	
	CH ₃ OH/C ₂ H ₅ OH	228-230	21,000	7 and 8
	CH ₃ OH or			
	C ₂ H ₅ OH or	226	18,000	9
	CH ₃ CN			
	H ₂ O	225	18,000	9
	Dioxane	230		This
	C ₂ H ₅ OH	227	21,000	Report

*The dielectric constants of the solvents are: n-hexane, 1.9; dioxane, 2.2; ethyl alcohol, 24; methyl alcohol, 33; acetonitrile, 39; and water, 79.

Compound	Solvent	λ_{\max} (nm)	ϵ_{\max}	Reference
<u>Nitrosamines</u>				
(CH ₃) ₂ N-NO	C ₂ H ₅ OH	231	7,000	12
		346	100	12
	Light petroleum	232	5,900	12
		351	98	
		361	125	
		374	105	
	H ₂ O	339	100	13
	C ₂ H ₅ OH	345*		
	<u>n</u> -Hexane	338sh		
		350		
		364*		
1-Nitroso -3,5-dinitro -1,3,5-triaza- cyclohexane	C ₂ H ₅ OH	377		
		365	48	7
		(See Fig 5)		

has been done on reactions of N-nitrosamines initiated by an $n \rightarrow \pi^*$ electronic transition (Refs 17-21) and their applications to natural products chemistry. The excited molecule, resulting presumably from the promotion of a nitrogen nonbonding electron, weakens the N-N bond increasing electron localization on the amine nitrogen and the oxygen atom of the nitrosamines (Ref 17). Irradiation of the nitramine solutions in the short wave UV range would provide an interesting comparison of the chemical reactivity of $\pi \rightarrow \pi^*$ transition in terms of bond-breaking steps if the latter occurs to the exclusion of $n \rightarrow \pi^*$ promotion as implied in the previous discussion of such spectra.

Among nitramines, dimethylnitramine presented one attractive instance of good solubility in solvents of such widely differing polarity as *n*-hexane and water as well as possible similarity of its photochemical reactions to those of HMX and RDX.

EXPERIMENTAL PROCEDURES

Materials

Redistilled 95% ethyl alcohol and Baker analyzed *n*-hexane were the solvents used. Dimethylnitramine was purified by recrystallization from aqueous alcohol followed by sublimation. N-Nitrosodimethylamine was obtained from Aldrich Chemical Company and used without further purification.

Procedure for Ultraviolet Irradiation

Ultraviolet light, chiefly of 254 nm wavelength, was obtained from a low pressure mercury lamp, helical in shape. Most of the irradiations were carried out with dimethylnitramine dissolved in 95% ethyl alcohol to give solutions in the 0.01-0.18 mole/liter concentration range. Before each irradiation, the 4-ml solution used was deaerated in a quartz spectrophotometer cell (5 cm X 1 cm path) which was modified with a stopcock attachment, and its absorption spectrum (210 - 385 nm) was recorded using a Beckman DK-1 UV-VIS spectrophotometer. The sample cell was then placed in a predetermined and reproducible position in front of the UV-lamp. At different times, the irradiation was interrupted, and the sample was transferred to the spectrophotometer to record any change in the absorption spectrum. Photolysis of the sample was then resumed as in the beginning. In the initial experiment, it was established

that, presumably because of a product, the optical density (O.D.) at a λ_{max} , of 345 nm increases linearly with the time of irradiation. Thereafter, only a minimum number of spectra were recorded up to a maximum of two hours in each run to confirm linearity of O.D. with time. To obtain a general picture of the kinetics, the intensity of the 345 nm band was measured as a function of irradiation time and concentration of the solute. Quantum yields were also estimated with actinometric measurements described below.

In the only other type of photolysis experiment the irradiation of dimethylnitramine was carried out in the solid form. For this experiment a thin layer of the sample held between the inside walls of a 0.5 cm (i.d.) quartz tube and a piece of glass rod, slightly smaller in diameter, was used. The tube with the sample was then placed centrally inside the spiral-shaped UV lamp. After evacuation in the normal way, irradiation was carried out for 2 hours.

Actinometry

The photoreduction of ferric to ferrous ion in an acidified potassium ferrioxalate was used to measure the light intensity to which the sample solution was to be exposed. A potassium ferrioxalate solution (4 ml, 6×10^{-3} molar in 0.1 N sulfuric acid) was substituted for the nitramine solution, irradiated for a fixed time, and mixed with 0.1% aqueous 1:10-phenanthroline and a sodium acetate buffer. A purple color is formed by ferrous ion, the concentration of which was determined from absorption at λ_{max} , 510 nm (ϵ_{max} , 11,110). A quantum yield (Φ) of 1.25 was used for $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ conversion in calculations of light quanta absorbed. The concentrations of the actinometer as well as the irradiated sample solutions were such that the incident light was totally absorbed. The Fe^{2+} ion figures shown in Table 2 were obtained in a series of three irradiations. The precision of the light intensity measurements was on the order of $\pm 6\%$.

Table 2 Actinometry

Irradiation		Fe ²⁺
Run No.		(mole/min X 10 ⁴)
1		3.72
		3.78
2		3.50
		3.46
3		3.94
		4.01
		4.05
Average		3.74 ± 0.3

Analysis of Products

The products could not be isolated for characterization since most of the irradiations were performed on a very small scale. Instead, several techniques were used to identify the principal product which appeared to be the same under a variety of experimental conditions. Samples of the irradiated alcoholic solution were directly analyzed by (besides UV absorption spectra) gas chromatography using a Perkin-Elmer Model-154D unit equipped with a flame-ionization detector. Dimethylnitramine and dimethylnitrosamine, which was the principal product in most of the experiments, were readily separable by a 6 ft x 1/4 in stainless steel column containing firebrick coated with Ucon Polyglycol (F.E. LB-550X) and operated at 140°C and 10 psig helium pressure. The elution times and peak areas were calibrated by the use of authentic samples.

The irradiated solid alone was analyzed by IR since the solvents used for solution photolysis were not suitable for IR. The spectra were obtained on a P.E. Model 621 Grating Spectrometer.

NMR spectra were obtained on a Varian T-60 instrument and the mass spectra by using a CEC 21-104 single focusing machine having a direct introduction probe.

Results of Photolysis of Dimethylnitramine in Alcohol Solution

As is Section 1 of this report shows, dimethylnitramine in ethyl alcohol solution exhibits a strong absorption in the 220 to 290 nm wavelength region with a maximum near 240 nm. Above 300 nm, it has a negligible absorption. Solutions in the 0.01 to 0.81 moles/l concentration range were irradiated with light of chiefly 254 nm wavelength for a period of two hours in most experiments. Spectrophotometric analysis from time to time showed a clear new absorption band at 345 nm which increased in intensity linearly with time under the above experimental conditions. The absorption spectra taken before and after the irradiation are shown together in Figure 6.

During the latter stages of each experiment, additional well defined maxima at 335 and 355 nm and two shoulders at 325 and 370 nm were also seen as Figure 6 shows. Further, it was observed that the λ_{max} at 240 increased in optical density slightly. From the UV absorption bands it appeared that one major product was N-nitrosodimethylamine which, in ethanol, shows two bands: λ_{max} -231 nm, E_{max} -7,000; and λ_{max} -346, E_{max} -100. At least one other product seems to have been formed on this basis although it has not been possible to identify it with available data.

Since product isolation seemed to be a difficult step in small scale experiments, several analytical techniques (described below) were employed to ensure identification of the principal product. In each case the irradiation experiment was modified to suit the particular analytical technique.

Gas Chromatography

The chromatographic instrument is described in the "Experimental Procedures" section of this report. This method was used for the irradiated alcoholic solution which was directly injected into the carrier gas stream. The identity and quantum yields were determined from the calibrated elution times and peak areas, respectively. Quantum yield for the disappearance of dimethylnitramine was found to be 0.34 and for formation of dimethylnitrosamine, 0.11.

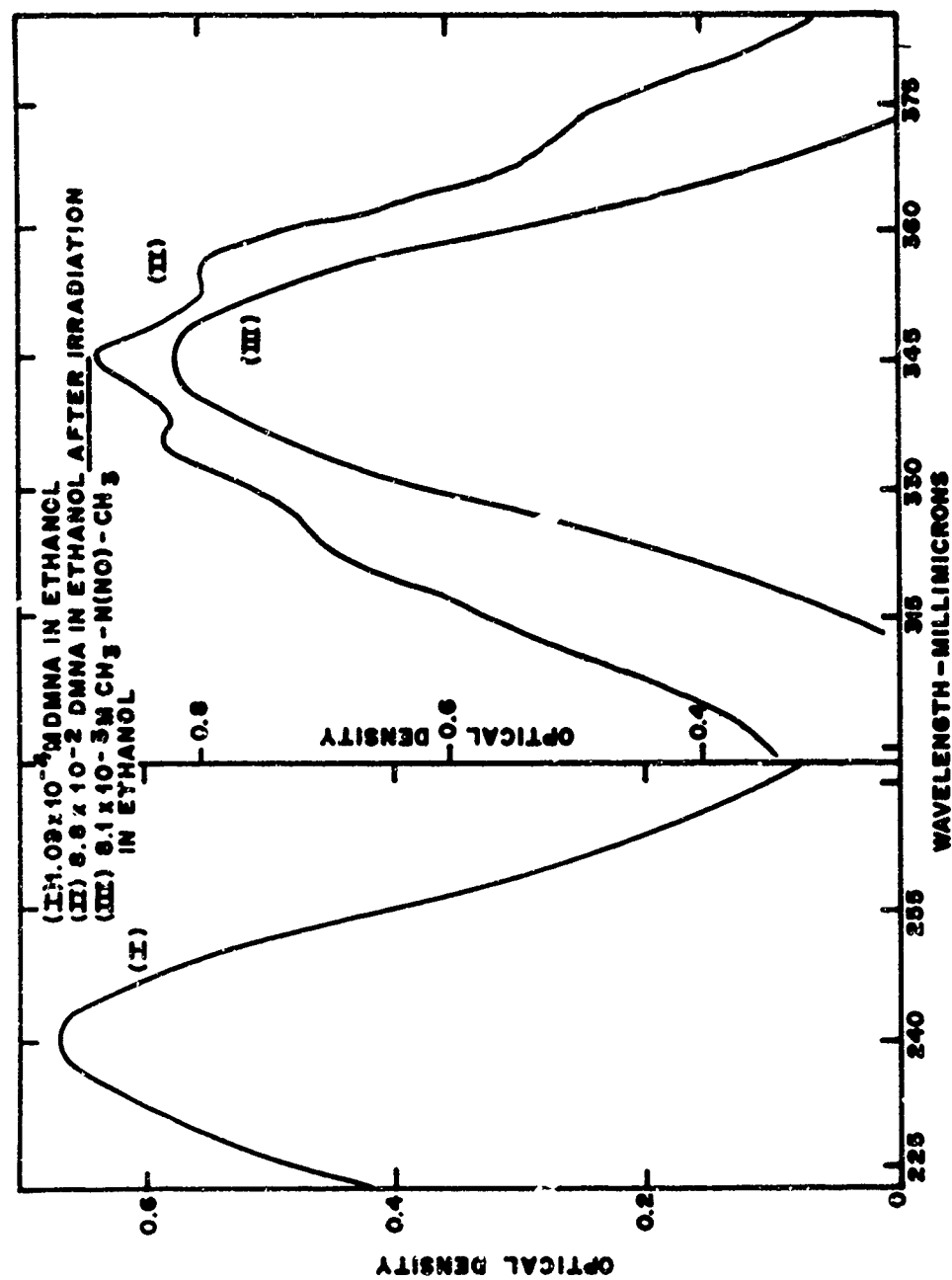


Fig 6 Absorption spectra of DMNA in alcohol solution, before and after irradiation

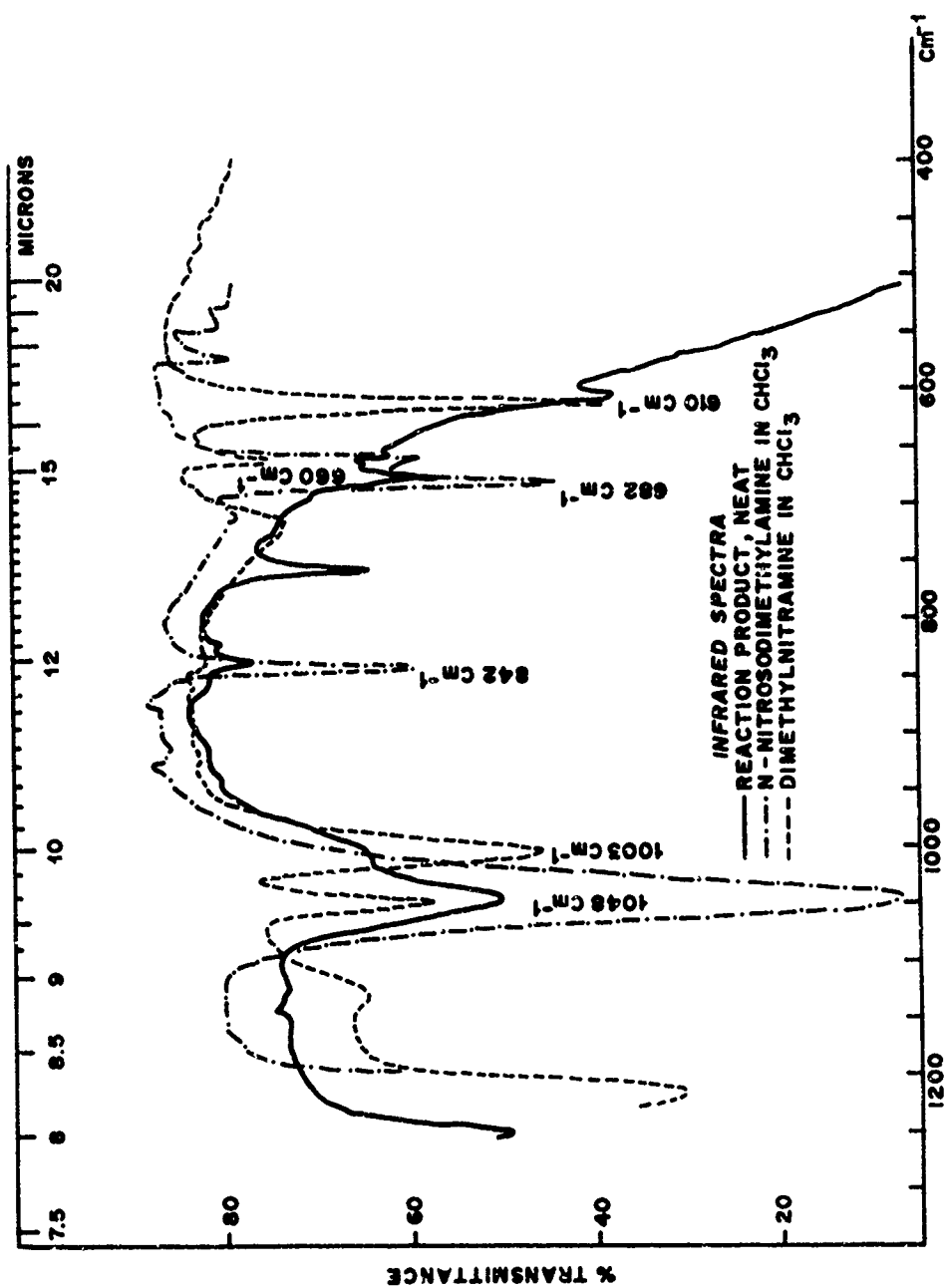


Fig 7 Infrared spectra of irradiated solid dimethylnitramine

NMR SPECTRAL DATA

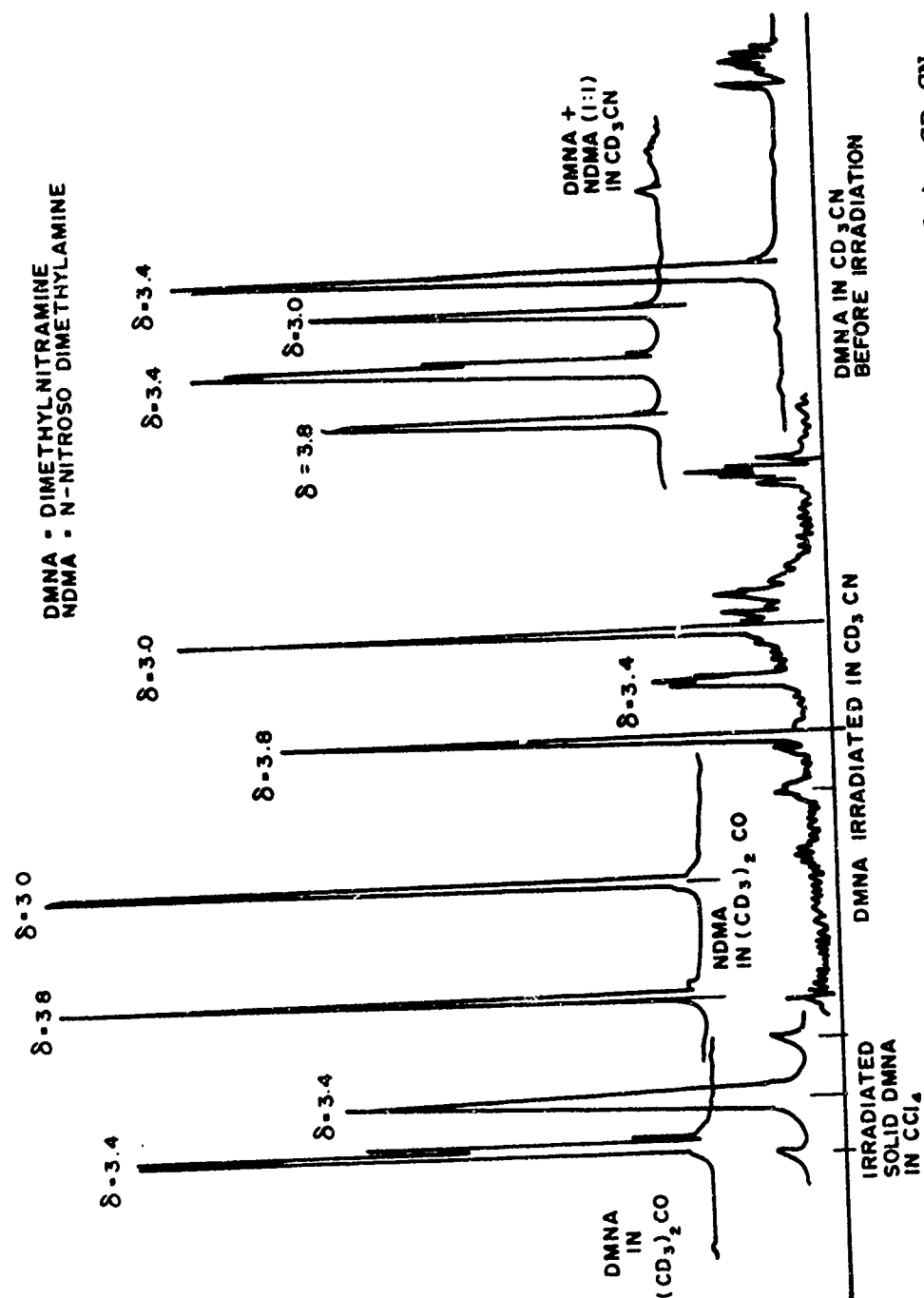


Fig 8 NMR spectra of irradiated DMNA and NDMA in $(CD_3)_2CO$ and in CD_3CN

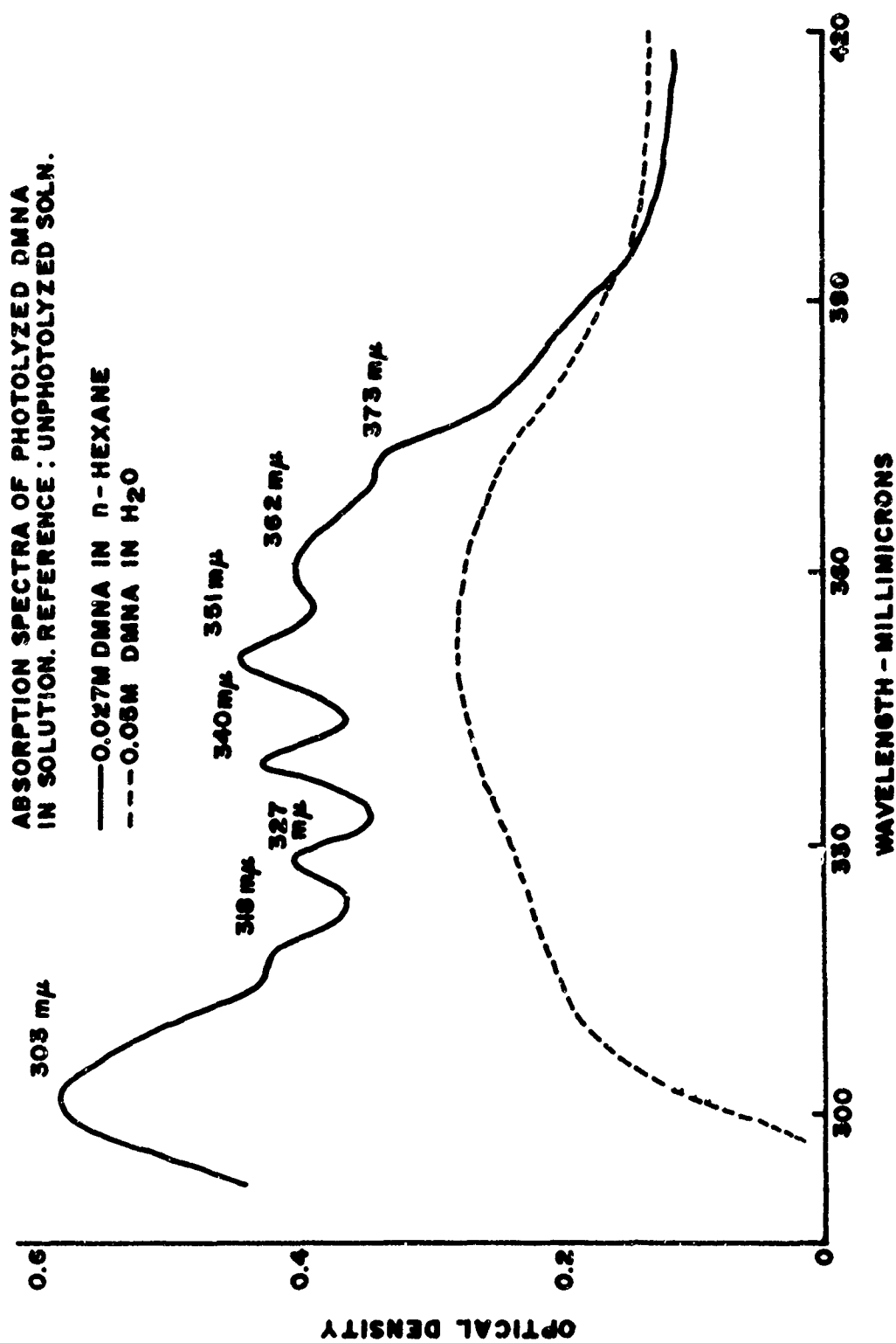


Fig 9 Absorption spectra of photolyzed DMNA in solution

IR Spectrum of Irradiated Solid Dimethylnitramine

Because the solvent had to be changed to obtain an IR spectrum, one irradiation was performed in the solid state after which the IR could be obtained readily. It was also hoped that any broad differences in the behavior of solid phase reaction will be seen in this experiment. The latter aspect was of importance since the general interest of the current program was in fact centered on photolysis of solid nitramines. After a two-hour irradiation of a polycrystalline sample as described in the experimental section, a yellow liquid resulted. A film of this liquid held between two NaCl plates was used to get the IR spectrum shown in Figure 7. The region between 1100-600 cm^{-1} clearly showed similarity to the spectrum of nitrosamine. A UV spectrum of the same yellow oily product also showed that the conversion of nitramine to nitrosamine was almost 44% and that the product giving rise to the other bands of irradiated alcoholic solution was not formed in this experiment.

NMR Spectra

(a) Irradiation of the solid: The NMR spectrum of the above photolyzed solid dimethylnitramine in CCl_4 showed a strong peak at $\delta = 3.40$ ppm corresponding to unreacted starting material and two peaks at $\delta = 3.77$ and 3.00 ppm, respectively. By comparison with a reference the latter two peaks were shown to be due to the formation of dimethylnitrosamine. The chemical shifts agreed with those reported by Axenrod and Milne (Ref 20). No other product was detected by this method.

(b) In a second experiment, a solution of dimethylnitramine in CD_3CN was outgassed and sealed in a quartz NMR sample tube. NMR spectra recorded before and after UV irradiation showed a diminished peak at 3.42 ppm and new peaks at 3.77 and 3.00 ppm, respectively, corresponding to the nitrosamine.

The relevant portions of the NMR spectra are shown in Figure 8. It is interesting to note that the proton signal from dimethylnitramine appears as a triplet in acetonitrile and acetone but as a singlet in CCl_4 . The coupling to the nitrogen is apparently weak.

Irradiation in n-Hexane Solution

N-Nitroso dimethylamine gives the $n \rightarrow \pi^*$ transition at 15 nm longer wavelength in n-hexane compared to a solution in alcohol. It should therefore, be possible to observe this shift by carrying out the irradiation in n-hexane as solvent provided it does not repress formation of the nitrosamine in the photolysis. Since this is also an incidental check on solvent participation in photolysis, it was decided to carry out some experiments in n-hexane. The results of one initial run using a 0.0274 M solution are described in Table 3 below.

Table 3 UV maxima above 300 nm in n-hexane.

$(CH_3)_2N-NO$	Irradiated n-hexane solution of DMNA
377 B	373 D
364 A	362 C
350 C	351 A
338 Sh	340 B
	303 A'
	318 Sh
	327 B'
	388 Sh

A, B, C, and D represent decreasing order of intensities of absorption maxima which belong to the nitrosamine; Sh=shoulder; DMNA= dimethylnitramine.

The absorption spectrum of the irradiated n-hexane solution of dimethylnitramine is presented in Figure 9. In the hope that water with a high dielectric constant would produce a shift of absorption bands in the opposite direction (hypsochromic), an experiment was run in aqueous solution also. However, the absorption spectrum included in Figure 9 was less revealing and helpful for identification.

The absorption bands corresponding to the N-nitroso-dimethylamine solution in n-hexane are shown in Table 3 along with the bands for the irradiated solution and their intensities. Although the spectrum is quite consistent with the presence of nitrosamine among the products, the distribution of intensities indicates one or more products with overlapping absorption bands. For example, the absorption

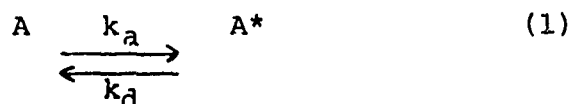
maxima of methyl nitrite which is not an unlikely product in this reaction, occur at 357, 345, 369, 333, 322, and 310 nm, in the order of decreasing intensity. Overlapping spectra of such mixtures will show an intensity distribution difficult to interpret with limited data. Further experiments already underway should make possible the identification of the remaining products but presumably, the net reaction after photolysis is different in n-hexane from that in alcohol.

To summarize the analytical data on the main product, dimethylnitrosamine its formation in solution photolysis was identified in three different solvents: in alcohol solution g.c. and UV absorption support its presence, in n-hexane the solvent shift on UV absorption bands supports its identity, and, in acetonitrile it was identified unambiguously by NMR. Its formation as a major photolysis product of solid was indicated by IR spectra and confirmed by NMR.

Kinetics and Concentration Dependence of Absorption at 345 nm

Preliminary kinetics were determined by measuring at 345 nm the increase of optical density with irradiation time. From the plots of optical density vs time, the average rate in each experiment was computed. A quantum yield for product formation could be calculated with the assumption that all absorption at 345 nm was due to N-nitrosodimethylamine. This was done at various initial concentrations of the nitramine shown in Table 4. The second and third columns in this table show the rates and the quantum yields, respectively.

Figure 10 shows that the rate of reaction increases almost linearly with concentration in the 0.01-.08 mole/l. range. At higher concentrations, it levels off. To consider the concentration dependence from a kinetic point of view, let Equations 1 and 2 represent the generalized photochemical steps that yield products when dimethylnitramine is irradiated:



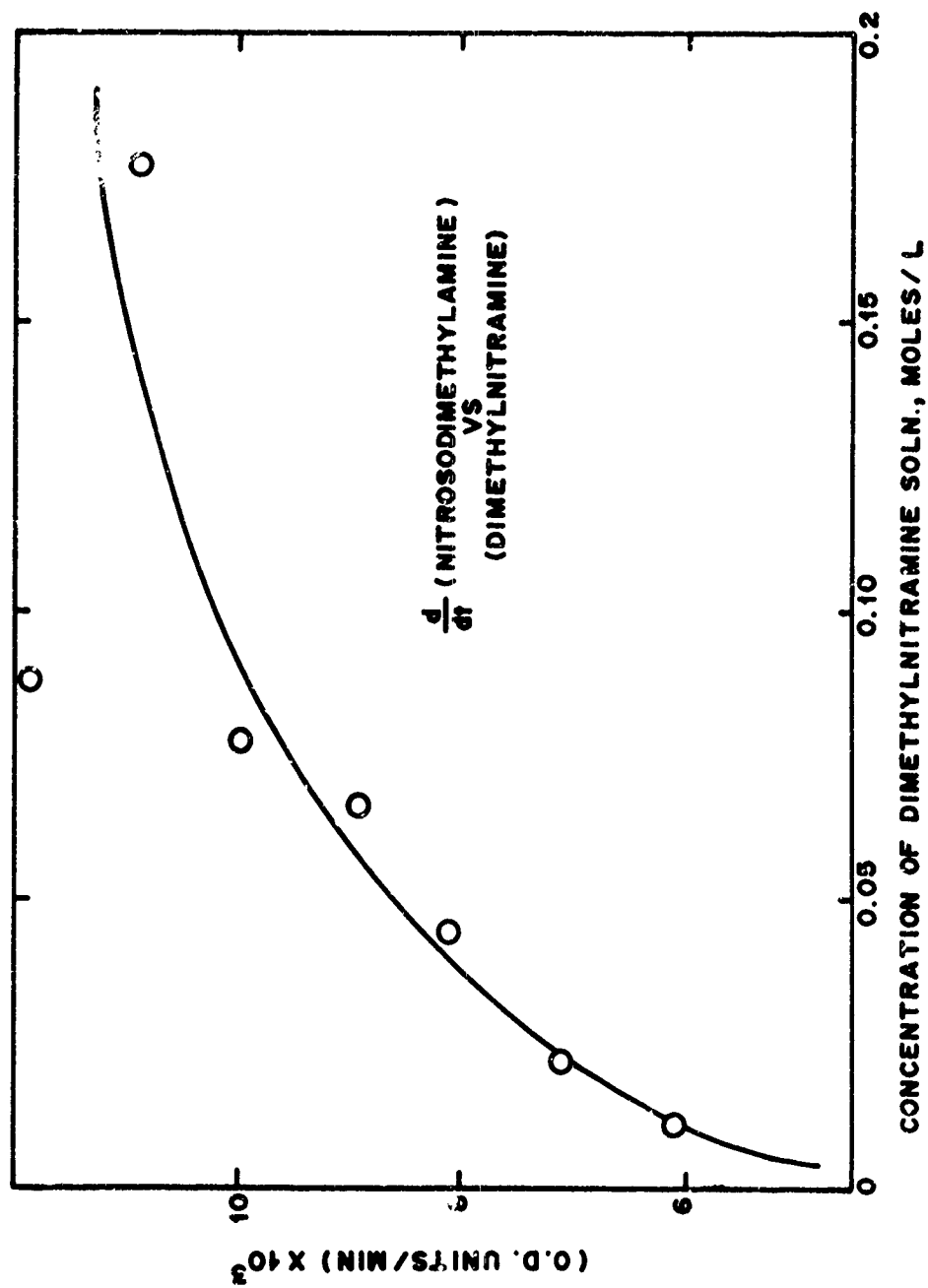


Fig 10 Rate of reaction vs concentration of DMNA in solution

$$\log \Phi_R = n \log (A) \quad A = \text{DMNA}$$

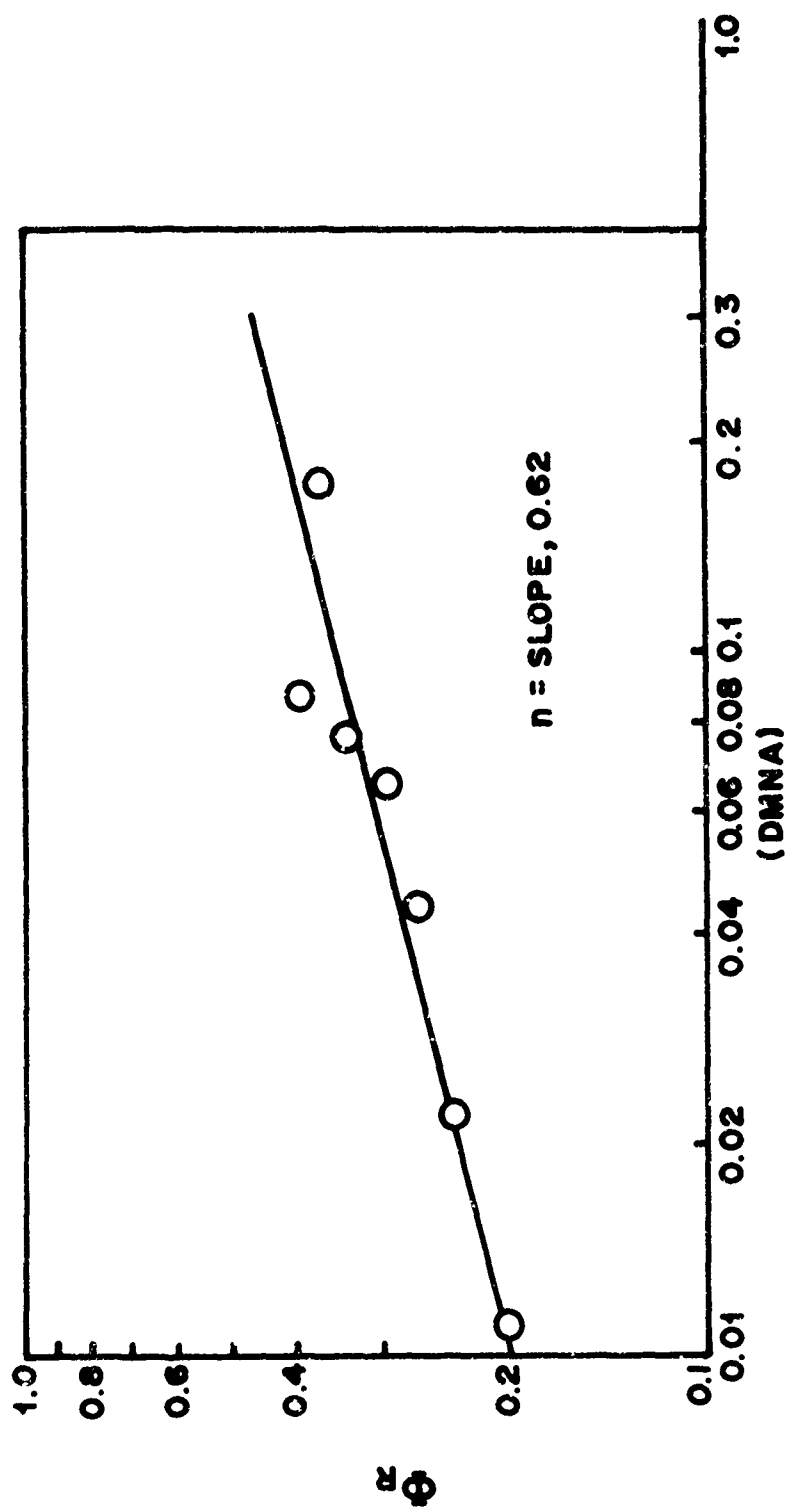


Fig 11 Plot of $\log [\Phi_R]$ versus $\log [\text{concentration}]$

Equation 1 is the photoactivation step giving A^* and k_d , an oversimplified sum of the rate constants of all deactivation modes of A^* other than the chemical reaction giving P in Equation 2. Deactivation returns A^* to the ground state. If ϕ_{A^*} is the quantum yield for the excitation and ϕ_r the quantum yield for the reaction which gives products, it can be shown that^a

The relative values of (A) , k_r , and k_d will determine the precise dependence of ϕ_r on the concentration of A; for example, at very low concentrations of A, if $k_d \gg k_r$, then a linear relation should result [$\phi_r = \phi_{A^*} k'(A)$]. On the other hand, if $k_d \ll k_r$, then ϕ_r will be essentially independent of (A) . Since the present results show an almost linear increase of ϕ_r with (A) in the 0.01 to 0.08 mole/l range, it implies that k_d is larger than k_r . At high concentration, it is to be expected that k_d would be severely affected by (A) . This is seen by the complicated relation that becomes evident as the concentration is increased beyond 0.08 mole/. The overall curve seems to represent a relation:

$$\phi_r = C (A)^{0.6} \quad (\text{Fig 11}).$$

Oxygen Effect

The possible effects of oxygen with a triplet ground state on the photoreaction were tested in a trial experiment by photolyzing on alcoholic (95%) solution (0.077 M) without degassing. After a 30 minute irradiation, the absorption spectrum of the solution was indistinguishable from that of an outgassed and irradiated solution. Dissolved oxygen, therefore, appears to have no noticeable effect on the reaction in the initial stages.

(a) The rate of activation to give excited species A^* could not depend on (A) since the concentration was high enough for complete absorption of light; it is proportional only to absorbed light intensity, I_{abs} . Therefore, using steady state approximations:

$$d(A^*)/dt = 0 = k_a I_{abs} - k_d(A^*) - k_r(A^*)(A)$$

$$(A^*) = k_a I_{abs} / [k_r(A) + k_d] = \phi_{A^*} / [k_r(A) + k_d]$$

$$d(P)/dt = \phi_r = k_r(A^*)(A) = \phi_{A^*} k_r(A) / [k_r(A) + k_d]$$

$$\phi_r = \phi_{A^*} [k_r(A)] / [k_r(A) + k_d] \quad (3)$$

Table 4

Photochemical yield of N-nitroso dimethylamine^a (NDMA) in 254 nm irradiation of dimethyl nitramine (DMNA) in 95% ethyl alcohol.

Concn. of DMNA, m/l	Rate of formation of NDMA (optical density units ^b at 345 nm per min) X10 ⁻³	Apparent quantum yield of NDMA c
0.011	6.06	0.20
0.022	7.10	0.24
0.044	8.09	0.27
0.066	8.90	0.30
0.077	9.96	0.34
0.088	11.90	0.40
0.177	10.80	0.36

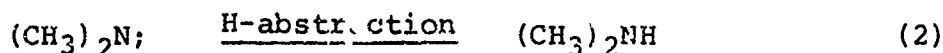
(a) With the assumption that the absorption maximum at 345 nm was all due to formation of NDMA

(b) Slopes of linear plots of optical density vs time which passed through the origin

(c) Based on 3.74×10^{-4} moles/min Fe^{2+} (Table 1) and a quantum yield, 1.25 for Fe^{2+} ion. Further, absorption by other products at 345 nm was not subtracted

DISCUSSION

Dimethylnitramine, whether irradiated in ethyl alcohol solution or in *n*-hexane, yields the corresponding nitrosamine as a major product. The chemical yield amounts to about 35% although the quantum yield is not very high. It can be safely assumed that monochromatic light (253.7 nm) causes a $\pi \rightarrow \pi^*$ transition in which an electron in the π bond is promoted to an antibonding π^* orbital. On the basis of solvent shift, no $n \rightarrow \pi^*$ transition occurs in the dialkyl nitramines as in the case of nitrosamines. In the nitrosamines, the transition results in a weakened N-N bond and leads to all the observed products. The $\pi \rightarrow \pi^*$ promotion, on the other hand, may be expected to increase the electron density on the N-N bond thereby increasing its bond strength. If such were the case, the N-N bond breakage will not be efficient. The kinetic data indicates that the nitrosamine could not have been formed in a simple one-step splitting of an oxygen atom. The increase in quantum yield with concentration is inconsistent with such a mechanism. It would be of obvious help in understanding the total photochemical reaction if one could determine whether or not the nitrosamine formed by means of the breakage of an N-N bond, as shown below:



The concentration dependence of the reaction rate in solution in fact points to bimolecular steps. The observation that irradiation in the solid state did not yield detectable products other than nitrosamine shows that the mechanism may be different. Here primary fragments of bond fission have a greater probability of recombining and solvent participation is absent.

In a previous brief study of the photolysis of nitramines (Ref 23), dibenzylnitramine in pentane solution and dibutylnitramine in trifluoroacetic acid were irradiated. UV-light which was mainly of a greater wavelength than ~280 nm was used. In the first case, the main products were dibenzylnitrosamine, N-benzylidene benzylamide,

and dibenzylamine nitrate. In the second case, because the solvent was a proton donor, the only product detectable was the nitrosamine. These observations can be explained on the basis of a hydrogen abstraction reaction by an initially formed radical similar to those of equations 1 and 2. Since dibutylnitramine does not absorb light above 280 nm, the reason for the formation of nitrosamine is not obvious though it may be due to the passing of a small amount of light from the 254 nm band through the pyrex walls.

In the present study of dimethylnitramine, experiments are underway using N^{15} as an isotopic tracer to find an answer to the question of why N-N bond breakage occurs in the photolytic reactions. Some preliminary N^{15} experiments with RDX and HMX have shown that two mechanisms may be operative simultaneously, one requiring N-N cleavage and the other without such a step.

Comparison of Photodecomposition with Thermal Decomposition

Photodecomposition of dimethylnitramine was similar to thermal decomposition in the gas phase with respect to one major product, dimethylnitrosamine. Gas phase decomposition in the temperature range, 165-2000 gives the nitrosamine in 80% yield. Flournoy (Ref 3) proposed a mechanism consisting of the first three of the following steps to which Korsunskii and Dubovitskii (Ref 4,5) added Equation 6 on



the basis of decomposition experiments with nitrosamine in the presence of NO_2 . Kinetic data strongly suggested that Equation 3, representing N-N bond breakage, was the rate determining step. A similar mechanism might be expected to be sensitive to oxygen. Trial runs show that oxygen has an effect on the n-hexane solution photolysis but not on the alcohol photolysis. To compare once again with the thermal decomposition of RDX and HMX, these cyclic nitramines were shown to undergo decomposition in the solid phase via predominant breakage of C-N bonds but not N-N bonds.

Table 5

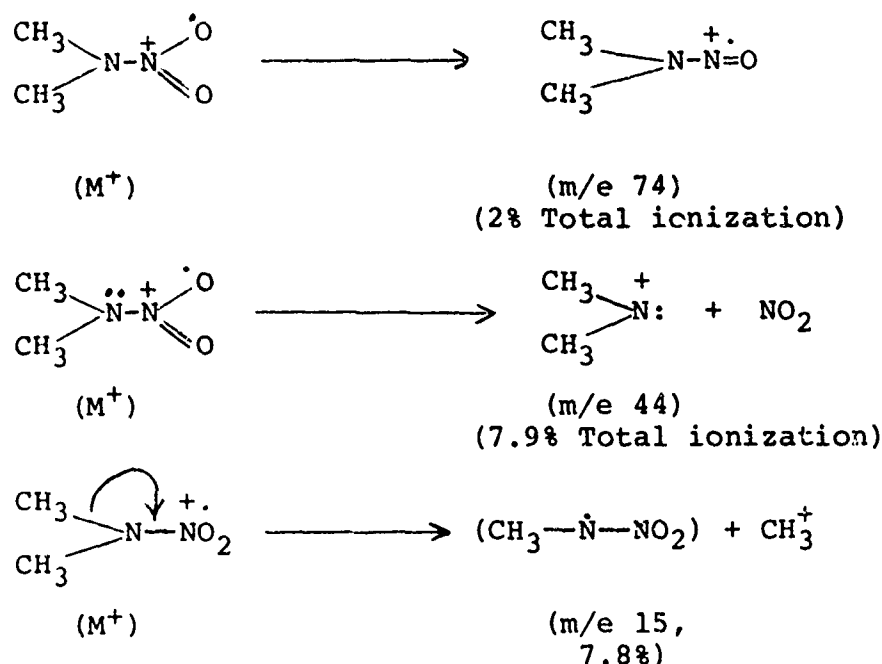
Mass spectral fragmentation pattern of dimethylnitramine

M. Wt. of $\text{CH}_3\text{N}(\text{NO}_2)\text{CH}_3$, 90; Instrument, CEC 21-104;
 Ionization Voltage 70 eV

<u>Mass/Charge Ratio</u>	<u>Relative Abundance</u>	<u>% Total Ionization</u>
12	0.5	
13	1.0	
14	4.3	
15	30.6	7.8
16	0.6	
17	0.6	
18	14.6	
26	0.4	
27	4.6	
28	3.7	
29	3.0	
30	19.8	
31	0.1	
32	2.6	
38	1.2	
39	1.9	
40	6.5	
41	7.3	
42	100	25.4
43	77.6	19.6
44	31.2	7.9
45	1.6	
46	1.8	0.46
59	0.6	
60	11.0	
61	0.3	
73	0.6	
74	9.9	2.5
75	0.4	0.1
89	0.2	
90	56	14.2
91	0.2	

Bond Fission in Electron-Impact Fragmentation

The mass spectral fragmentation of some secondary nitramines including dimethylnitramine were also reported recently (Ref 6) by P. Catinny, and their prominent ions were identified with the help of isotopic tracers and/or high resolution mass measurement. Among the ions formed under electron impact from dimethylnitramine those with $m/e = 15, 44, 74$, and 75 are helpful in judging the relative efficiency of N-N and C-N bond cleavages when the ionization yield is taken into account. Fragmentation of the parent ion ($m/e = 90$) was extensive as evidenced by its low ionization yield (14%). Mass spectral peaks with their relative abundance and the ionization yields of some relevant ions are shown in Table 5. The proposed structures of 74 and 44 fragments and the postulated reactions giving them are as follows:



The N-O bond seems to cleave with very much lower efficiency than the N-N bond. The ion at $m/e \ 75$ (Table 5) simply represents the loss of a methyl group, i.e., $(M - \text{CH}_3)^+$, formed by a C-N bond breakage. Although its yield was only 0.1%, CH_3^+ ion ($m/e \ 15$) appeared in 7.8% ionization equal to that of mass 44 ion. This shows that among the one-step (before rearrangement) bond breaking reactions the N-N and C-N bond cleavages are of equal efficiency

while N-O bond also cleaves to a smaller extent. In the case of RDX, however, the N-N bond seemed to undergo cleavage very efficiently judging from the high (23%) ionization yield of NO_2^+ which, in fact, was the base peak.

CONCLUSIONS

In summary, the gas phase thermal decomposition of dimethylnitramine appears to proceed by N-N bond breakage in a primary rate determining step and subsequent reformation of the same bond giving nitrosamine in good yield. The electron impact fragmentation also in the gas phase, gives less discriminating cleavage reactions where both C-N and N-N bonds break with equal efficiency and N-O to a minor extent. Absorption of UV-light of wavelength 253.4 nm results in excitation of a pi-electron to an antibonding orbital which may result in a slight increase of electron density between the nitrogen atoms. However, it appears to give reactions which are superficially similar to the thermal degradation of dimethylnitramine since dimethylnitrosamine is the main product under various experimental conditions. The energy in a 253.7 nm photon is equivalent to 112 K Cal/Mole and, if localized in one bond this is enough energy to cause breakage of any one of the bonds in the molecule under study. The excited species from an $n-\pi^*$ promotion in nitrosamines has more of a biradical nature and a weakened N-N bond. Fission of the latter followed by rearrangements in the presence of acids gives alkylidene derivatives and oximes. In the present photolysis experiments, other products to be identified, should help elucidate steps and shed light on the precursor species in the excited state.

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<p>This report reviews the absorption spectra of several nitramines and gives new spectra for dimethylnitramine, RDX, and HMX. It also deals with the photolysis of dimethylnitramine in alcohol solution.</p> <p>Solvent shifts in the absorption spectra support the conclusion that dimethylnitramine undergoes a $\pi-\pi^*$ electronic transition caused by intense absorption in the near UV (240 nm) and exhibits weak absorption in n-hexane up to 318 nm, probably due to excitation of nonbonding electrons in the nitramino groups. Although the solvent chosen for this study was ethyl alcohol, some data are presented from photolysis in acetonitrile and γ-hexane, as well as from irradiation in the solid form. G.C., NMR, IR, and UV techniques were used for product analysis. The major photolysis product of dimethylnitramine under the experimental conditions used appears to be N-nitrosodimethylamine, as in gas-phase thermal decomposition. In alcohol solution, its rate of formation increases considerably and later levels off with increasing initial concentration of dimethylnitramine. The overall photodecomposition is compared with previous thermal decomposition and electron-impact fragmentation data in terms of bond-breaking steps. Quantum yields for disappearance of dimethylnitramine and formation of nitrosamine are 0.3 and 0.1, respectively.</p>		

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